

PTO 03-4185

CY=JA DATE=19860313 KIND=A
PN=61-050929

METHOD FOR REFINING VINYL COMPOUNDS
[Biniru Kagobutsu no Seisei Hoho]

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UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D. C. July 2003

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(10): JA
DOCUMENT NUMBER	(11): 61050929
DOCUMENT KIND	(12): A
	(13): PUBLISHED UNEXAMINED APPLICATION (Kokai)
PUBLICATION DATE	(43): 19860313
PUBLICATION DATE	(45):
APPLICATION NUMBER	(21): 59170009
APPLICATION DATE	(22): 19840816
ADDITION TO	(61):
INTERNATIONAL CLASSIFICATION	(51): C07C 7/12; B01J 20/02; C07C 11/02, 11/12, 15/44
DOMESTIC CLASSIFICATION	(52):
PRIORITY COUNTRY	(33):
PRIORITY NUMBER	(31):
PRIORITY DATE	(32):
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TITLE	(54): METHOD FOR REFINING VINYL COMPOUNDS
FOREIGN TITLE	[54A]: Biniru Kagobutsu no Seisei Hoho

[Translator' note: The specification on pages 207 to 209 was amended and replaced by the specification on pages 210 to 212, part of which was again amended and replaced by the description found on pages 213 to 214.]

1. Title

A Method for Refining Vinyl Compounds

2. Claims

A refining method characterized by the fact that a vinyl compound mixture that contains acetylene compounds is brought into contact with an adsorbent that contains monovalent or zero-valent copper and/or silver that is supported by a carrier so as to adsorb and eliminate the acetylene compounds in the mixture with the adsorbent.

3. Detailed Description of the Invention

(Industrial Field of Application)

The present invention pertains to a method for refining vinyl compounds. More specifically, it pertains to a method for refining vinyl compounds according to which an adsorbent that contains monovalent or zero-valent copper and/or silver that is supported by a carrier is brought into contact with a vinyl compound mixture that contains acetylene compounds so as to adsorb and eliminate the acetylene compounds.

* Number in the margin indicates pagination in the foreign text.

[Prior Art]

As a commonly known method for refining and eliminating a trace quantity of acetylene compounds contained in a vinyl compound, there is, for example, a method disclosed in JP-A-S58-210852, according to which a vinyl compound containing a trace quantity of acetylene compounds is brought into contact with a catalyst in the presence of hydrogen so as to selectively hydrogenate the acetylene compounds, thus refining and eliminating them.

It is common knowledge that acetylene compounds react with copper and/or silver to yield acetylated copper and/or acetylated silver (see, for example, "Fiza Saishin Yuki Kagaku I [Feezer's Current Organic Chemistry I]," Maruzen, 2nd Edition, p.264.)

(Problems that the Invention Intends to Solve)

These techniques, however, have the following problems.

First, with respect to the method of refining and eliminating acetylene compounds by selective hydrogenation, the hydrogenation reaction of vinyl compounds cannot be prevented, and, as a consequence, alkyl compounds are produced as byproducts. If it is not desirable for these byproduct alkyl compounds to be present in vinyl compounds, this method requires a further refining process, such as distillation separation, etc., thus rendering itself uneconomical.

With respect to the method that refines and eliminates acetylene compounds in the form of acetylated copper or silver, acetylated copper or silver thus formed is unstable and, in some cases, could

have explosive properties, thus presenting a problem in handling. Furthermore, the produced precipitation must be isolated, thus making the process more complex.


The present inventors assiduously studied these refining methods and, as a result, found a method that makes it possible to eliminate acetylene compounds from an acetylene-compound-containing vinyl compound mixture easily and safely and also without forming alkyl compounds as byproducts, thus achieving the present invention.










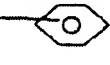
(Means of Solving the Problems)

The present invention is a refining method characterized by the fact that a vinyl compound mixture that contains acetylene compounds is brought into contact with an adsorbent that contains monovalent or zero-valent copper and/or silver that is supported by a carrier so as to adsorb and eliminate the acetylene compounds in the mixture with the adsorbent.

The acetylene compounds mentioned in the present invention are represented by General Formula $RC \equiv CH$, and R here represents a hydrogen atom or a hydrocarbon having up to 10 carbon atoms. Some examples include $CH \equiv CH$, $CH_3C \equiv CH$, $C_2H_5C \equiv CH$, $C_3H_7C \equiv CH$, $(CH_3)_2CHC \equiv CH$, $C_4H_9C \equiv CH$, $C_5H_{11}C \equiv CH$, $C_6H_{13}C \equiv CH$, $C_7H_{15}C \equiv CH$, $C_8H_{17}C \equiv CH$, $C_9H_{19}C \equiv CH$, $C_{10}H_{21}C \equiv CH$, $CH_2 = CHC \equiv CH$, $C_{[illegible]}H_{[illegible]} \equiv CH$, and the like. Even if the substituent R contains a nitrogen atom and/or oxygen atom, it does not pose any problem. Some examples of this case

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include $\text{HC} \equiv \text{CCOOCH}_3$, $\text{HC} \equiv \text{CCH}_2\text{OH}$, $\text{HC} \equiv \text{CCH}_2\text{COOH}$, $\text{HC} \equiv \text{CCH}_2\text{N}(\text{CH}_3)_2$, $\text{HC} \equiv$
 $\text{CCH}(\text{CH}_3)\text{NHCH}(\text{CH}_3)_2$, $\text{HC} \equiv \text{CCH}(\text{OH})\text{CH}_3$, $\text{HC} \equiv \text{CCH}(\text{OH})\text{C}_4\text{H}_5$, $\text{HC} \equiv \text{CCH}_2 -$ ,
 $\text{HC} \equiv \text{CCONH}_2$, $\text{HC} \equiv \text{CCOOH}$, and the like.

The vinyl compounds in the present invention are those that have one or more vinyl groups, and some examples include $\text{CH}_2 = \text{CH}_2$, $\text{CH}_3\text{CH} = \text{CH}_2$, $\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2$, $(\text{CH}_3)_2\text{CHCH} = \text{CH}_2$, $\text{C}_3\text{H}_7\text{CH} = \text{CH}_2$, $\text{CH}_3\text{CH} = \text{CHCH}_3$, $\text{C}_2\text{H}_5\text{CH} = \text{CHCH}_3$, $\text{C}_4\text{H}_9\text{CH} = \text{CH}_2$, $\text{C}_3\text{H}_7\text{CH} = \text{CHCH}_3$, $\text{C}_2\text{H}_5\text{CH} = \text{CHC}_2\text{H}_5$, $(\text{CH}_3)_2\text{CHCH} = \text{CHCH}_3$,
 $(\text{CH}_3)_2\text{CHCH}_2\text{CH} = \text{CH}_2$, $(\text{CH}_3)_2\text{CCH} = \text{CH}_2$,  $\text{CH} = \text{CH}_2$,  $- \text{CH} = \text{CH}_2$,
 $- \text{C}(\text{CH}_3) = \text{CH}_2$,  $- \text{CH} = \text{CHCH}_3$, $\text{CH}_3 -$  $- \text{CH} = \text{CH}_2$, $(\text{CH}_3)_2 -$  $-$
 $\text{CH} = \text{CH}_2$, $\text{C}_2\text{H}_5 -$  $- \text{CH} = \text{CH}_2$, $\text{C}_2\text{H}_5 -$  $- \text{CH} = \text{CH}_2$ [sic], $(\text{C}_2\text{H}_5)_2 -$  $-$
 $\text{CH} = \text{CH}_2$, $\text{CH}_2 = \text{C} = \text{CH}_2$, $\text{CH}_2 = \text{C} = \text{CHCH}_3$, $\text{CH}_2 = \text{CHCH} = \text{CH}_2$, $\text{CH}_2 =$
 $\text{CH}(\text{CH}_3)\text{CH} = \text{CH}_2$, $\text{CH}_2 = \text{CH} -$  $- \text{CH} = \text{CH}_2$, and the like., and a vinyl compound mixture here indicates a mixture that contains one or more of the aforesaid vinyl compounds.

An adsorbent containing carrier-supported monovalent or zero valent copper and/or silver that can be used in the present invention can be prepared by causing a carrier to support one or more kind of inorganic salt, organic salt, or oxide of copper and/or silver and by reducing them with an appropriate reducing agent.

As the carrier, various kinds of metal oxides, active carbon, etc., can be used, of which alumina, silica, active carbon, etc., are

especially preferable. As for the composition, the ratio of copper and/or silver to the carrier is selected from a range of 1 to 48 % by weight, preferably from a range of 5 to 30 % by weight. No specific limitation is imposed on the method for preparing the adsorbent, and conventionally employed support methods can be used as appropriate. According to one example method, the adsorbent can be prepared as follows. After an alumina carrier is impregnated with a specified quantity of a solution of an acid- or water-soluble salts, such as copper chloride, copper nitrate, copper acetate, copper sulfate, etc., this copper salt is heated at a high temperature in air or in an inactive gas that contains oxygen. Thereafter, this copper oxide is reduced to a monovalent or metal-form copper by a dry or wet method, using an appropriate reducing agent, such as hydrogen, hydrazine, formaldehyde, sodium formate, etc.

There is no strict requirement with regard to the reaction conditions for carrying out the method of the present invention, but, generally speaking, the reaction is conducted under the following conditions.

The reaction temperature can be selected from a temperature range of -10 to 150° C, preferably from a range of 0 to 100° C. If the reaction temperature is too high, the polymerization of vinyl compounds progresses, which is not desirable. When the vinyl compound mixture containing acetylene compounds assumes the form of a gas at the aforesaid reaction temperature, the space velocity (gas flow

rate/catalyst quantity) can be selected from a range of 1,000 to 100,000 Hr⁻¹, preferably from a range of 4,000 to 50,000 Hr⁻¹. When the mixture is a liquid at the aforesaid reaction temperature, the LHSV [liquid hourly space velocity] can be selected from a range of 0.1 to 80 Hr⁻¹, preferably from a range of 1 to 30 Hr⁻¹. There is no specific limitation imposed on the quantity of acetylene compounds contained in the vinyl compound mixture, and acetylene compounds can be eliminated even when their concentration is in the range of 10⁻⁴ to 10 % by weight. With respect to the reaction mode for implementing the method of the present invention, a fixed-bed reaction is preferable, and both fluidized-bed mode and overflow mode can also be used here, but the present invention is not limited to these. ✓

(Effects of the Invention)

With the method described in the foregoing, acetylene compounds contained in a vinyl compound mixture can be eliminated easily and safely, without producing alkyl compounds as byproducts.

(Working Examples)

The following presents some working examples of the present invention, but the present invention is not limited to these.

Preparation of Adsorbent

Preparation of Adsorbent (A)

290 g of copper nitrate trihydrate was dissolved in 318 g of water, to which solution was added 318 g of γ-alumina, and the mixture was evaporated and concentrated over a water bath. The obtained

copper-salt-supporting substance was baked at 600° C in air for 3 hours and subjected to a reducing process for 2 hours at 200° C in a hydrogen flow, thereby obtaining a copper-supporting alumina adsorbent (A). (A)

Preparation of Adsorbent (B)

12 g of silver nitrate was dissolved in 32 g of water, to which /212 solution was added 32 g of γ -alumina, and the mixture was evaporated and concentrated over a water bath. The obtained silver-salt-supporting substance was baked at 600° C in air for 3 hours and subjected to a reducing process for 2 hours at 200° C in a hydrogen flow, thereby obtaining a silver-supporting alumina adsorbent (B).

Preparation of Adsorbent (C) (B)

30 mL of active carbon that had been dried for 3 hours at 150° C was packed in a column having an inner diameter of 8 mm, and 40 mL of ethanol in which was dissolved 6 g of copper (I) chloride was poured into the column. Thereafter, a reducing process was carried out at 200° C for 2 hours in a hydrogen flow, thereby obtaining a copper-supporting active carbon adsorbent (C).

Working Example 1

In a column having an inner diameter of 8 mm, 30 mL of Adsorbent A was packed, and a 1,3-butadiene mixture containing 1000 ppm ethyl acetylene and 1000 ppm vinyl acetylene was run through the column at room temperature under a gauge pressure of 10 kg/cm² at an LHSV of 5

Hr⁻¹. After the liquid was run through the column for one hour, a sample was taken, and its composition was analyzed. As a result, the aforesaid acetylene compounds were not detected.

Working Example 2

Tests were conducted with Adsorbents B and C in the same manner as in Working Example 1, and a sample was taken after the liquid was run through the column for one hour, and the composition was analyzed. As a result, no acetylene compound was detected.

Working Example 3

In the same manner as in Working Example 1, a column having an inner diameter of 8 mm was filled with 30 mL of Adsorbent A.

A gas comprised of ethylene that contained 100 ppm of acetylene was passed through the column at room temperature under normal pressure at an SV of 5,000 Hr⁻¹. After the gas flowed through the column for one hour, the composition analysis was carried out. As a result, no acetylene was detected.

Working Example 4

A gas comprised of propylene that contained 100 ppm of methyl acetylene was processed in the same manner as in Working Example 3. After the gas flowed through the column for one hour, the composition analysis was carried out. As a result, no methyl acetylene was detected.

Working Example 5

A styrene mixture comprised of styrene that contained 50 ppm of phenyl acetylene was processed in the same manner as in Working Example 1, except that the pressure used was normal pressure and that the LHSV was 10 Hr^{-1} . A sample was taken after the liquid was run through the column for one hour, and the composition was analyzed. As a result, no phenyl acetylene compound was detected.